



# High efficiency production of substitute natural gas from biomass

Luc P.L.M. Rabou\*, Lex Bos

Energy research Centre of the Netherlands, PO Box 1, 1755 ZG Petten, The Netherlands

## ARTICLE INFO

### Article history:

Received 1 December 2010

Received in revised form 22 July 2011

Accepted 17 October 2011

Available online 28 October 2011

### Keywords:

Biomass

Gasification

Methanation

Hydrodesulphurization

Hydrogenation

## ABSTRACT

The Energy research Centre of the Netherlands (ECN) is developing technology for the production of Substitute Natural Gas (SNG) from biomass with 70% efficiency. An essential step in the process is the removal of thiophene, while benzene and toluene must be retained and converted into methane. Experimental results are presented which show that thiophene can be reduced from 10 ppmv to 0.1 ppmv by commercial hydrodesulphurization (HDS) catalysts at atmospheric pressure. The catalysts also promote the water gas shift and hydrogenation reactions. The operating temperature of 550 °C is too high and the Gas Hourly Space Velocity (GHSV) of 100 h<sup>-1</sup> too low for practical application. Future SNG installations will operate at higher pressure, which should promote the catalytic activity at lower temperature and result in higher GHSV values. The catalyst used for conversion of benzene did work initially, but degraded within 50 h.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

The conversion of biomass into Substitute Natural Gas (SNG) is an attractive option for densely populated areas where direct application of biomass for heating is not favoured because of logistic problems and concerns about emissions. Transport, distribution and heat generation are more efficient, less cumbersome and often cheaper for gas than for biomass. However, the conversion process from biomass to SNG does involve costs and energy loss which should be minimized. The Energy research Centre of the Netherlands (ECN) is developing MILENA gasifier technology [1] for SNG production with the aim to reach an energetic efficiency of at least 70% from biomass to SNG. Fig. 1 shows schematically what a future system could look like.

The production of SNG from biomass starts with the conversion of biomass into syngas or producer gas. Both contain CO, H<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O, but producer gas also contains a considerable amount of CH<sub>4</sub> and other hydrocarbons. In order to meet natural gas quality standards, the combustible components have to be converted with the use of catalysts into CH<sub>4</sub>. At some stage, CO<sub>2</sub> and H<sub>2</sub>O have to be removed. In the methanation step, part of the gas heating value is lost, i.e. converted to heat. The loss in heating value is larger for syngas than for producer gas, because the latter needs only partial conversion.

The efficiency difference between syngas and producer gas routes to SNG can be as large as 10%abs, even if the efficiency is

corrected for the SNG equivalent of electricity which is used or exported [2]. However, the higher efficiency of the producer gas route comes at the price of more elaborate gas cleaning. The main culprits are unsaturated and (poly)-aromatic hydrocarbons (= tar) which are easily converted into carbon by Ni methanation catalysts.

The amount of tar can be reduced to some extent by the use of excess steam. However, that increases the heat demand and reduces the efficiency of the gasifier. ECN is developing the MILENA gasifier technology which uses little steam, because ECN is confident that its OLGA technology [3,4] can remove tar effectively. Light aromatic compounds like benzene (C<sub>6</sub>H<sub>6</sub>) and toluene (C<sub>7</sub>H<sub>8</sub>) and unsaturated hydrocarbons like ethylene (C<sub>2</sub>H<sub>4</sub>), which represent a significant part of the producer gas heating value (see Table 1), remain in the gas.

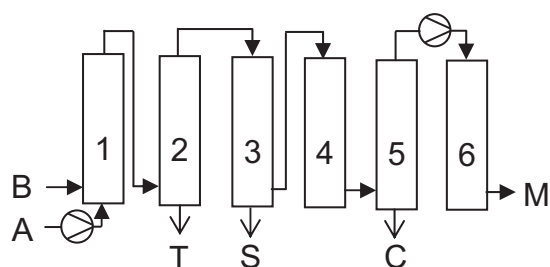
To prevent problems in the methanation step, ECN aims at hydrogenation and pre-reforming of these compounds, i.e. conversion into C<sub>2</sub>H<sub>6</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>. The alternative would be to separate them from producer gas and find a different application. Combustion to deliver process heat does not fit the heat balance of the MILENA gasifier.<sup>1</sup> Selling as chemical feedstock could be an attractive option, but probably only at large scale.

Pre-reforming and methanation require the use of catalysts which are sensitive to poisoning by sulphur compounds in producer gas. The allowed total sulphur concentration is in the region of 10–100 ppbv. Even if clean wood fuel is used, producer gas will contain hundreds of ppmv H<sub>2</sub>S, tens of ppmv COS, 10 or more

\* Corresponding author. Tel.: +31 224564467; fax: +31 224568487.

E-mail addresses: [rabou@ecn.nl](mailto:rabou@ecn.nl) (L.P.L.M. Rabou), [a.bos@ecn.nl](mailto:a.bos@ecn.nl) (L. Bos).

<sup>1</sup> For a gasifier with higher heat demand, combustion of the separated compounds will be advantageous if otherwise producer gas would be burned. However, such a gasifier cannot deliver the high SNG efficiency aimed at by ECN.



**Fig. 1.** High-efficiency SNG system consisting of (1) gasifier, (2) tar removal, (3) gas cleaning, (4) pre-reformer, (5) CO<sub>2</sub>/H<sub>2</sub>O removal, (6) methanation. Main streams: A = air, B = biomass, T = tar, S = sulphur + chlorine, C = CO<sub>2</sub> + H<sub>2</sub>O, M = CH<sub>4</sub> + H<sub>2</sub>O.

**Table 1**  
Main components in MILENA producer gas by volume and by energy content.

| Component(s)                                                     | Volume fraction (%) | Energy fraction (%) |
|------------------------------------------------------------------|---------------------|---------------------|
| CO + H <sub>2</sub>                                              | 37                  | 38                  |
| CH <sub>4</sub>                                                  | 8                   | 25                  |
| C <sub>2</sub> H <sub>m</sub> ( <i>m</i> = 2, 4, 6) <sup>a</sup> | 3                   | 17                  |
| C <sub>n</sub> H <sub>m</sub> (3 ≤ <i>n</i> ≤ 7) <sup>b</sup>    | 0.8                 | 13                  |
| Tar                                                              | 0.35                | 7                   |
| H <sub>2</sub> O                                                 | 31                  | –                   |
| CO <sub>2</sub> (+N <sub>2</sub> )                               | 20                  | –                   |

<sup>a</sup> Mainly C<sub>2</sub>H<sub>4</sub>.

<sup>b</sup> Mainly C<sub>6</sub>H<sub>6</sub>.

ppmv of thiophene (C<sub>4</sub>H<sub>4</sub>S), a few ppmv of thiols (CH<sub>3</sub>SH, C<sub>2</sub>H<sub>5</sub>SH) and even smaller amounts of thiophene derivatives which contain one or more methyl-group(s) or benzene ring(s). Most of the lighter compounds can be removed easily, tar-like compounds can be removed by OLGA. Thiophene can be removed by adsorbents, but valuable benzene and toluene are adsorbed simultaneously. Selective thiophene removal by hydrodesulphurization (HDS) would be the preferred option, if it would work in producer gas.

In oil refineries, HDS catalysts are applied to convert thiophenes into sulphur-free hydrocarbons and H<sub>2</sub>S by reaction with H<sub>2</sub>. Conditions and requirements differ markedly from those for biomass producer gas: reactions occur in liquid instead of in gas, thiophene concentrations can be 10–100-fold higher at both entrance and exit, and the H<sub>2</sub> pressure is 30 bar or more.

Most present-day biomass gasifiers operate near atmospheric pressure. The MILENA gasifier can be designed for operation at 5–10 bar, but even then the partial H<sub>2</sub> pressure will be at most 3 bar. Raising the thiophene and H<sub>2</sub> partial pressures by producer gas compression is not an attractive option. It requires gas cooling and removal of water, which is needed to produce H<sub>2</sub> for the catalytic reactions and to suppress carbon formation. That is why we try to establish whether thiophene can be converted at lower pressures. This article presents results for conversion of thiophene in producer gas by commercial HDS catalysts at atmospheric pressure.

## 2. Experimental

The MILENA gasifier is an allothermal gasifier with separate reactors for gasification and combustion. Heat is generated in the combustion reactor by combustion of char, which is produced in the gasification reactor by pyrolysis of biomass. Char and heat are transported from one reactor to the other by bed material, which is usually sand or olivine. Bed material in the combustion reactor is fluidized by air which is needed for combustion. Bed material in the gasification reactor is fluidized by steam and by gas emanating from the biomass on heating. Usually, a steam to biomass weight ratio of 1:10–1:5 is used.

The experimental layout in the laboratory was similar to the one shown in Fig. 1, but without CO<sub>2</sub> removal or compressors. The

gas cleaning (part 3 in Fig. 1) actually consisted of an HDS reactor followed by three reactors with commercial adsorbents for HCl, H<sub>2</sub>S and COS. Except for the gasifier, all reactors and gas pipes were made of stainless steel 316. Commercial SNG production will require pressurized operation of at least the methanation section. In the laboratory tests, methanation at atmospheric pressure just served to check whether the gas cleaning was adequate.

Biomass producer gas was obtained from a 30 kW<sub>th</sub> MILENA gasifier which operated at about 850 °C and atmospheric pressure. Beech wood chips with 8% moisture were used as fuel. Small amounts of CO<sub>2</sub> were used as carrier gas for the steam and as shielding gas for the biomass transport screw. For the experiments only 10–20% (about 1 m<sub>n</sub><sup>3</sup> h<sup>−1</sup>) of the producer gas flow was used. Dust was removed by a hot gas filter kept at 450 °C. Tar was removed by the lab-scale OLGA system described in [3]. The gas was reheated from 90 °C at the OLGA exit to about 300 °C at the top entrance of the HDS reactor.

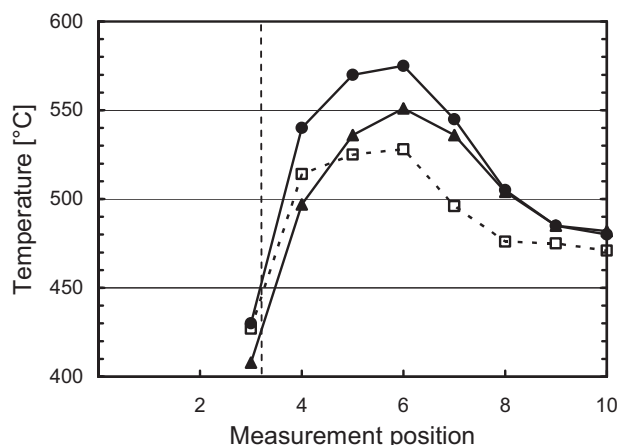
The HDS reactor had an inner diameter of 110 mm and a height of 1000 mm. The reactor wall was heated externally to a temperature between 350 °C and 475 °C. The upper part of the reactor vessel was empty, to allow further heating of the gas by contact with the heated wall. The reactor was filled with HDS catalyst pellets to a height of 400–800 mm, i.e. to a volume of 3.8–7.6 L. Commercial CoMoO catalyst pellets were used as delivered by two different suppliers. The nominal compositions were 3–5% CoO and 10% MoO<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> and 1–10% CoO and 10–20% MoO<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub>, respectively. Temperatures inside the reactor were measured by thermocouples, placed at 100 mm intervals in the reactor.

After steam addition and removal of chlorine and sulphur, the gas passed through four reactors with pre-reforming and methanation catalysts. These reactors had an inner diameter of 56 mm and a height of 520 mm. The reactor walls were heated externally to temperatures between 250 °C and 450 °C. The reactors were filled with catalyst pellets to a height of 120–200 mm, i.e. to a volume of 0.3–0.5 L. Temperatures inside the reactors were measured by thermocouples, placed at 30 or 70 mm intervals in and above the catalyst beds. The pre-reforming catalyst was selected in screening tests, but is no longer available. The methanation catalyst was a commercial Ni type. These catalysts were activated by pre-treatment with H<sub>2</sub>.

Gas analysis was performed with gas sensors for CO, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> and O<sub>2</sub>, and with a micro gas chromatograph (μGC) for the main components listed in Table 1 (except H<sub>2</sub>O and C<sub>3</sub> to C<sub>5</sub> hydrocarbons) plus Ar, H<sub>2</sub>S and COS. The Ar concentration in producer gas was negligible, but a small amount was added to determine the producer gas flow rate. The gas sampling was switched at ~30 min intervals between positions along the HDS to methanation train. Concentrations of C<sub>3</sub> to C<sub>5</sub> hydrocarbons, H<sub>2</sub>S, COS, thiophene and thiols were determined by analysis of gas sampled in Tedlar bags with a gas chromatograph (GC). Calibration of the GC showed that a detection limit of 0.05–0.1 ppmv could be obtained for sulphur compounds if sufficient care was taken to prevent contamination.

Concentrations of sulphur compounds like methyl-thiophene and benzo-thiophene and of nitrogen compounds like (methyl)-pyridine were determined by a method derived from the solid phase adsorption (SPA) method for tar [5]. A gas volume of 0.1 L is passed through a column containing 0.1 g amino phase adsorbent (SPE LC-NH<sub>2</sub>). The adsorbed sulphur and nitrogen compounds are extracted with di-chloro-methane and the solute analysed by GC/MS-SIM.

The sampling method was checked by passing the gas through two columns in series. When hot gas was sampled, the second column contained a significant fraction of thiophene and methyl-thiophenes, negligible fractions of benzo-thiophene, di-benzo-thiophene and pyridine, and none of methyl-pyridine or (iso)quinoline. The extraction procedure was checked by



**Fig. 2.** Temperature profiles (entrance to exit) over HDS reactor for different GHSV and reactor wall heating values. ( $\square$  =  $70 \text{ h}^{-1}$  at  $425/475^\circ\text{C}$ ,  $\bullet$  =  $65 \text{ h}^{-1}$  at  $450/475^\circ\text{C}$ ,  $\blacktriangle$  =  $40 \text{ h}^{-1}$  at  $450/475^\circ\text{C}$ ). The dotted line marks the front edge of the catalyst bed.

depositing known amounts of 8 sulphur compounds on the SPA material, leaving the material at room temperature for half an hour, followed by extraction and analysis. The recovery was 70–80% for thiophene and methyl-thiophene, about 90% for benzo-thiophene and 100% for the heavier compounds.

The results for thiophene and methyl-thiophene are similar to those for benzene and toluene: because of their volatility they are not captured quantitatively nor retained by the SPA material at room temperature or above. Pyridine and methyl-pyridine bind more strongly to the SPA material. Hence, they are captured and retained more easily.

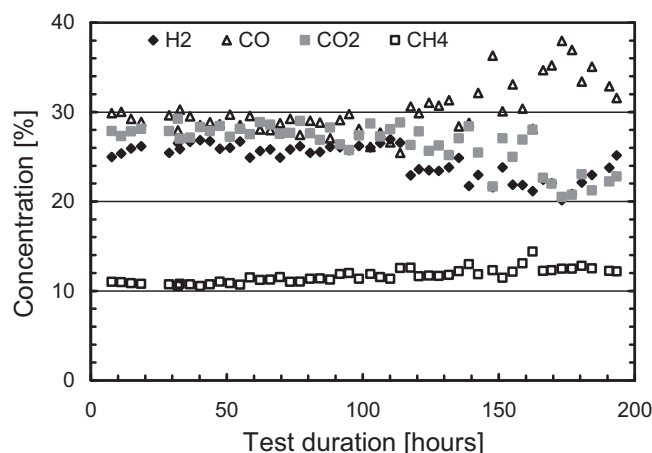
The detection limit for the sulphur compounds was about 0.02 ppmv and for the nitrogen compounds about 0.1 ppmv. Results for lighter compounds are less reliable because they are not captured quantitatively. Concentrations of  $\text{NH}_3$  and  $\text{HCN}$  were determined by trapping in acid and alkaline solutions, followed by chemical analysis of the solutions. The water concentration was mainly derived from the mass balance, but also checked by absorption on  $\text{P}_2\text{O}_5$  and weight measurement of the condensate obtained on cooling to  $5^\circ\text{C}$ .

### 3. Results

#### 3.1. HDS performance

Because of the large difference between standard applications and our tests, the catalyst suppliers could not give indications on the conditions to use and the performance to expect. The first tests made clear that CoMoO shows hardly any catalytic activity below  $350^\circ\text{C}$ , except for COS hydrolysis. True,  $\text{C}_2\text{H}_2$  was also removed, but probably by carbon formation and not by hydrogenation to  $\text{C}_2\text{H}_4$ . At higher temperature, the catalyst seemed to become active simultaneously for water gas shift (WGS), hydrogenation of  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$ , and conversion of thiols.

The heat evolved by WGS and hydrogenation reactions and the lack of active cooling of the HDS reactor, made the temperature in the reactor rise to  $550^\circ\text{C}$  or more. According to one of the suppliers, the catalyst should be able to withstand such temperatures, as the catalyst preparation already involves a high-temperature treatment. In the second part of the reactor, the temperature decreased, probably by heat loss in the absence of exothermic reactions. Fig. 2 shows temperature profiles for different Gas Hourly Space Velocities (GHSV) and settings of the reactor heating. When the heating was set at  $450^\circ\text{C}$  for the first half of the reactor and  $475^\circ\text{C}$  for the second half, the amount of thiophene removed varied from 98%



**Fig. 3.** Concentrations of  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{CH}_4$  in dry producer gas at HDS entrance during 200 h test.

at  $\text{GHSV} = 65 \text{ h}^{-1}$  to 99.5% at  $\text{GHSV} = 40 \text{ h}^{-1}$ . When the heating for the first half of the reactor was reduced by  $25^\circ\text{C}$ , the removal efficiency decreased to 93% at  $\text{GHSV} = 70 \text{ h}^{-1}$ . A catalyst sample from another supplier gave nearly identical results. The GHSV values were calculated from the total catalyst volume. Given the temperature difference between the centre and edges of that volume and the temperature dependence of the catalytic activity, the GHSV values are probably underestimated by at least a factor 2. Still, the GHSV values remain too low for practical purposes.

Results from the gas analysis did not prove unambiguously whether or not the catalyst was active for methane formation or methane reforming. The amount of methane hardly changed, but was also close to methanation equilibrium with  $\text{CO}$  and  $\text{H}_2$  at the average temperature in the centre of the catalyst bed.

Thiols were removed more easily than thiophene. The limited amount of data for other compounds showed that when thiophene was removed (nearly) completely, the same held true for  $\text{HCN}$ , pyridine and methyl-pyridine, while  $\text{NH}_3$  was not affected. Concentrations of methyl-thiophene, benzo-thiophene, dibenzo-thiophene and methyl-dibenzo-thiophene were always too close to the detection limit to make definite statements, but the HDS catalyst did seem to remove these compounds at least partly.

HDS catalysts usually require sulphidation to become active. In our experiments, the state of sulphidation did not seem to affect the catalyst activity. One CoMoO sample absorbed  $\text{H}_2\text{S}$  completely for about 50 h. After 100 h,  $\text{H}_2\text{S}$  just passed through. From the  $\text{H}_2\text{S}$  concentration in the feed gas (about 150 ppm) and the gas flow, the sulphur uptake was calculated to be 1.5–2% on weight basis of the active material (0.22% relative to the total weight). Another sample, which was supposed to contain only CoMoO, evolved a lot of  $\text{H}_2\text{S}$  over the first hours of operation, strongly suggesting the sample actually contained CoMoS. Within a day the catalyst reached a stable state in which  $\text{H}_2\text{S}$  was neither adsorbed nor desorbed. The amount of sulphur released was calculated to be 1–1.5% on weight basis of the active material (0.2% relative to the total weight). In both cases, the catalytic performance did not seem to change during sulphur uptake or release. Neither was there any noticeable difference in performance between two samples with such different histories.

As the operating temperature of the HDS catalyst was considerably higher than usual, there were doubts about its stability. Several tests were performed to monitor the performance over 6–8 days of operation. Due to the complexity of tests with real producer gas, it was difficult to keep the gas composition and flow constant. The results can be seen in Figs. 3 and 4, which show the

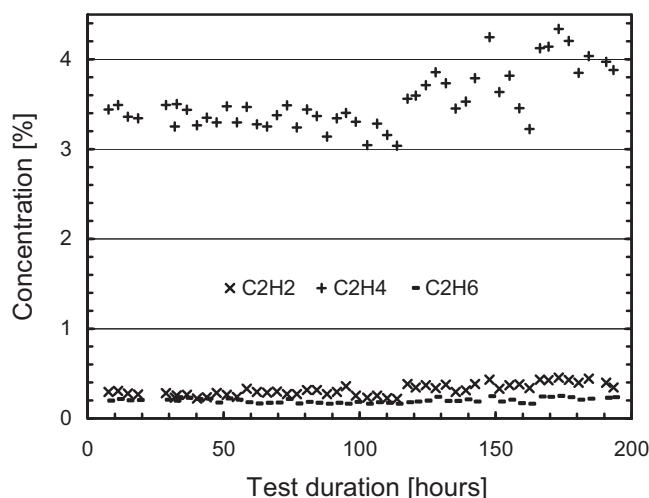


Fig. 4. Concentrations of  $C_2H_2$ ,  $C_2H_4$  and  $C_2H_6$  in dry producer gas at HDS entrance during 200 h test.

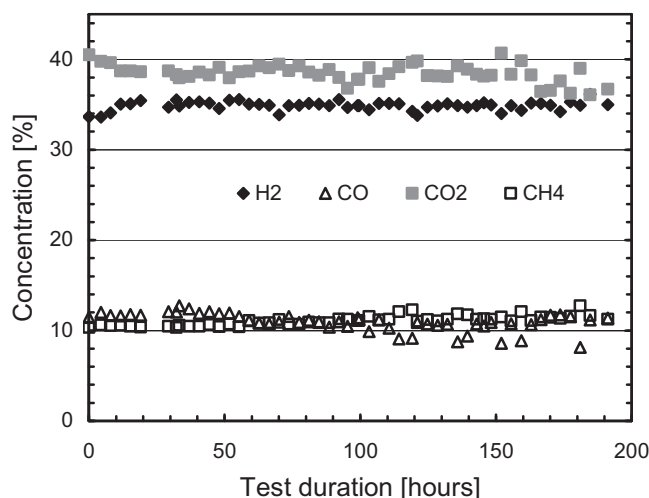


Fig. 5. Concentrations of  $CO$ ,  $H_2$ ,  $CO_2$  and  $CH_4$  in dry producer gas at HDS exit during 200 h test.

gas composition at the HDS reactor entrance. Despite changes and fluctuations due to operating problems in the second half of the test, the gas composition at the HDS reactor exit remained nearly constant (see Figs. 5 and 6).

A small but gradual increase of the  $C_2H_4$  concentration at the HDS reactor exit can be seen, possibly resulting from catalyst

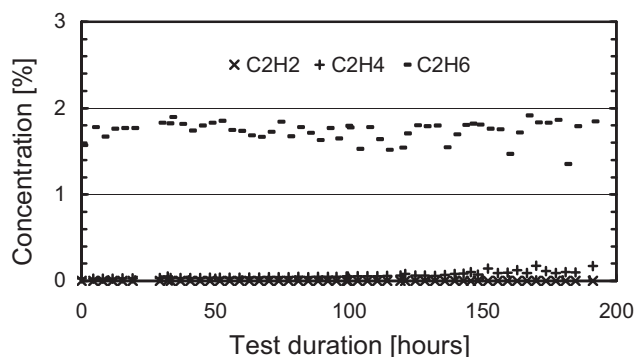


Fig. 6. Concentrations of  $C_2H_2$ ,  $C_2H_4$  and  $C_2H_6$  in dry producer gas at HDS exit during 200 h test.

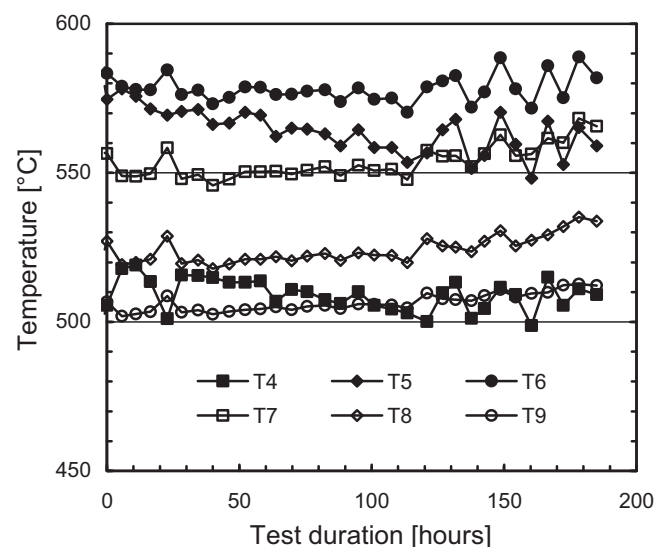


Fig. 7. Temperatures in HDS catalyst bed at positions 4–9 during 200 h test. Position 4 is close to the catalyst bed's front edge, position 9 close to the trailing edge.

degradation. However, the simultaneous decrease in  $CO$  concentration rather points to a lower temperature in the most active region. The temperature measurements showed a tendency to lower temperatures in the first half of the catalyst bed and to higher temperatures in the second half (see Fig. 7). These changes indicate, that heat is generated deeper in the catalyst bed. That might be due to a decreasing flow (compare the temperature curves at  $GHSV = 65 \text{ h}^{-1}$  and  $40 \text{ h}^{-1}$  in Fig. 2), but more probably is caused by decreasing catalyst activity.

### 3.2. Pre-reformer performance

The first tests were performed with producer gas not treated by the HDS catalyst and without steam addition. The pre-reforming catalyst did remove unsaturated and aromatic hydrocarbons, but only for a very short time. With the HDS reactor upstream converting ethylene and with steam addition to suppress carbon formation, the performance of the pre-reforming catalyst did improve markedly. Benzene and toluene were converted completely. According to the mass balance based on the gas analysis, the products were mainly gases and not solid carbon. The catalyst also converted  $C_2H_6$  and promoted the WGS and methanation reactions. As a result of exothermic reactions, the temperature in the reactor increased from 400 to 500 °C. Despite our efforts to remove sulphur compounds and suppress carbon formation, catalyst activity was lost within a few days (see Fig. 8). Whether the poor performance was still due to insufficient steam, the type of catalyst used or the high operating temperature is subject to further research.

### 3.3. Methanation performance

The deactivation of the pre-reformer did seem to have little influence on the performance of the three methanation reactors. The quick temperature rise and flat temperature profile in the first two reactors showed, that equilibrium was reached within a volume of 0.1 L at a total gas flow of  $1.2 \text{ m}_n^3 \text{ h}^{-1}$ . The exit gas compositions remained constant, apart from fluctuations caused by operating problems upstream. After the third methanation reactor, the gas contained less than 0.1%  $CO$ . The gas still contained about 8%  $H_2$ . Operation at higher pressure is required to achieve more complete conversion with  $CO_2$  into  $CH_4$ .

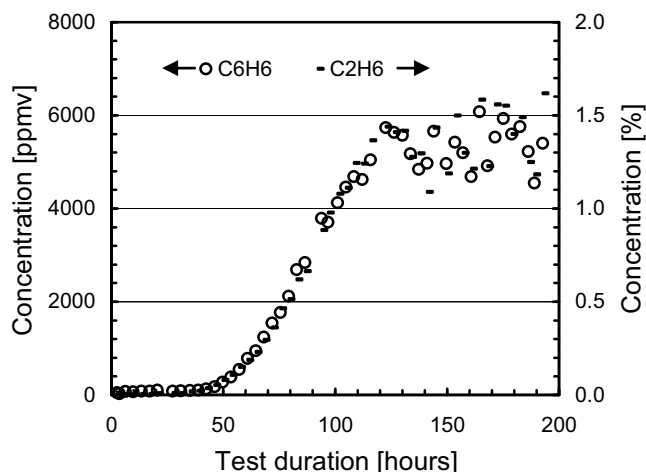


Fig. 8. Concentrations of  $C_6H_6$  (left axis) and  $C_2H_6$  (right axis) in dry producer gas at the pre-reformer exit.

#### 4. Discussion and conclusions

High-efficiency production of bio-SNG requires the conversion of biomass producer gas with a considerable amount of benzene into methane. To make that possible, thiophene has to be removed first. The present work shows that commercial CoMoO HDS catalysts are able to break down thiophene. The catalyst also promotes water gas shift and hydrogenation of  $C_2H_4$ . At atmospheric pressure an operating temperature of  $550^\circ\text{C}$  and gas hourly space velocity of  $100\text{ h}^{-1}$  are required to reduce the thiophene concentration from 10 ppmv to 0.1 ppmv. The temperature is probably too high for long-term catalyst stability and the space velocity too low from a cost perspective.

Research performed 30–40 years ago shows that considerable improvement can be obtained by operation at higher pressure [6,7]. As we expect that the MILENA gasifier in the future will be able to operate at 5–10 bar pressure, further research on thiophene removal by HDS will also consider that pressure region.

The high efficiency from biomass to SNG aimed for, requires that benzene and toluene in producer gas are separated and utilized as chemical feedstock or converted to  $CH_4$ . Test results for benzene conversion are encouraging, but catalyst activity is lost far too quickly, even when the concentration of sulphur compounds has been reduced to sub-ppm levels. The performance of different catalysts will be investigated and the effect of additional steam.

#### Acknowledgement

The research reported was financially supported by the Dutch Ministry of Economic Affairs.

#### References

- [1] C.M. van der Meijden, H.J. Veringa, B.J. Vreugdenhil, A. van der Drift, *International Journal of Chemical Reactor Engineering* 7 (2009) A53.
- [2] C.M. van der Meijden, H.J. Veringa, L.P.L.M. Rabou, *Biomass & Bioenergy* 34 (2010) 302–311.
- [3] P.C.A. Bergman, S.V.B. van Paasen, H. Boerrigter, in: A.V. Bridgwater (Ed.), *Pyrolysis and Gasification of Biomass and Waste*, CPL Press, Newbury, United Kingdom, 2003, pp. 347–356.
- [4] H. Boerrigter, S.V.B. van Paasen, P.C.A. Bergman, J.W. Könemann, R. Emmen, A. Wijnands, Report ECN-C-05-009, 2005.
- [5] C. Brage, Q. Yu, G. Chen, K. Sjöström, *Fuel* 76 (1997) 137–142.
- [6] S.P. Bhatia, *Canadian Journal of Chemical Engineering* 49 (1971) 605–610.
- [7] J.A. Wilkins, *Kinetics and interactions of the simultaneous catalytic hydrodenitrogenation of pyridine and hydrodesulphurization of thiophene*, PhD thesis Massachusetts Institute of Technology, 1977.